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Toxic Organic Emissions from Synfuels and Related Industrial Wastewater Treatment Systems

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Waste Water	Coal Gasification	Stationary Sources	13H
Water Treatment	Liquefaction	Synthetic Fuels	07D
Organic Compounds	Shale Oil		07C 08G
Emission	Coke		14G
Toxicity	Petrochemistry		06T

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ABSTRACT

The study examined the potential for toxic organic emissions from synfuels wastewater treatment systems. The synthetic fuels facilities examined were coal gasification, direct and indirect coal liquefaction, shale oil, by-product coke, and associated petrochemical products. A literature survey was performed to assess the fate of organic priority pollutants during wastewater treatment. Pollutants in the volatile fraction and base-neutral and acid extractable fractions were examined in order to assess their potential for volatilization during wastewater treatment. Compounds found to contribute organic emissions during wastewater storage and treatment were in the volatile fraction (e.g., benzene, toluene) and the base-neutral fraction (e.g., polynuclear aromatic hydrocarbons). Acid extractables (e.g., phenol) also present in synfuels wastewaters are rarely stripped or volatilized from wastewater stored in impoundments or during activated sludge treatment. However, phenol will be stripped from wastewaters that are applied to evaporative cooling towers as makeup water.

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LIST OF ABBREVIATIONS

AGR	— Acid Gas Removal
BHC	— Benzene Hexachloride
DEA	— Diethyl Amine
F-T	— Fischer-Tropsch (Synthesis)
H_A	— Henry's Law Constant
K	— Kelvin (absolute temperature)
KT	— Koppers-Totzek Indirect Coal Liquefaction
LPG	— Liquefied Petroleum Gas
MIS	— Modified In Situ Retort
PCB	— Polychlorinated biphenyl
PCTM	— Pollution Control Technical Manual
P_{ow}	— Octanol/water partition coefficient
SNG	— Substitute Natural Gas
TOC	— Total Organic Carbon
VOC	— Volatile Organic Compounds

SECTION 1

INTRODUCTION

Air emissions from industrial wastewater treatment processes pose a potential environmental concern where these emissions cannot be effectively controlled. Volatilization of organic compounds from surface impoundments is one source of concern. It is also possible that aeration during activated sludge processes may cause air stripping of volatile organics and increase emissions to the atmosphere. At this time, the fate of toxic organics in industrial wastewater handling and treatment processes is uncertain. An accurate assessment of their fate during and after wastewater treatment must be made before assessing the need for emission control. Therefore, there is a need to compile available information that establishes the magnitude of the problem.

The purpose of this study is to assemble data from the literature on the the fate of toxic organics during aerobic wastewater treatment. Data on the competitive interactions between biodegradation, air stripping, vaporization, and bioaccumulation in waste sludge are also included. The emphasis is on synfuels facilities such as coal gasification, direct and indirect liquefaction, and shale oil which may produce liquid fuels and petrochemicals.

The report is organized into seven sections. Excluding the introduction, these sections are:

Section 2: Summary and conclusions;
Section 3: Studies on toxic organic emissions from wastewater treatment processes;
Section 4: Process descriptions and methods of wastewater treatment;
Section 5: The presence and fate of volatile organic compounds in

wastewaters from synfuels industries;

Section 6: Data limitations, gaps, and research needs; and

Section 7: References.

SECTION 2

SUMMARY AND CONCLUSIONS

The coal gasification, direct and indirect coal liquefaction, shale oil, by-product coke, and associated petrochemical products all produce wastewaters which contain organic priority pollutants. Little actual data are available as to the exact nature of the organics and their concentrations at present, since many of these processes are still being developed or the data are considered proprietary. The wastewater treatment processes which will be used in future commercial-scale facilities are also uncertain at this time.

A literature survey was performed to assess the actual fate of organic priority pollutants during wastewater treatment. The results reveal that little information is available at present with which to define the magnitude of this problem. Although it has long been believed that the reduction in effluent concentration of organics is due to biodegradation, there is a possibility that some pollutants may also be adsorbed onto sludge, volatilized, or forcibly stripped during treatment. Several studies have been performed to attempt to assess their fate; however, progress has been slow towards resolving the questions concerning the actual fate of pollutants during wastewater treatment. Some researchers have also attempted to develop theoretical models to predict the fate of the organics; however, the results to date have been inconclusive. The ability to predict fates and resultant concentrations in the different phases (i.e., solid, liquid, gas) present in wastewater treatment applications is doubtful without a concerted effort to develop an experimental program that will accurately track pollutant fate during treatment so that the models can be verified with test data.

Most of the models available estimate only the maximum emissions of certain compounds. They also do not take into consideration the competition

between air stripping, biodegradation, and accumulation in sludge. The accuracy of the estimation is unknown, for in many cases, no data are available with which to compare the predictions. Some laboratory studies have been performed with synthetic wastes in an attempt to experimentally determine the fate of organics. However, the few compounds studied were present in concentrations lower than those which are usually found in high-strength industrial wastes. This may lend error to the analysis, since a compound may bioaccumulate in systems containing high pollutant concentrations but be entirely biodegraded in systems with lower concentrations.

No one removal mechanism may be examined by itself without causing inaccuracies in experimental data. For example, if removal by air stripping is the only process considered, the estimated air emissions may be higher than the actual, since some compounds are also preferentially biodegraded (e.g., methylene chloride) at low concentrations. This lends error to the prediction of the fate of the compound.

Based on the data found through the literature survey, many EPA priority pollutants may present a hazard due to volatilization and air stripping during wastewater treatment. Most of the volatile fraction pollutants (i.e., EPA 624) and several of the base-neutral fraction pollutants, particularly simple halogenated compounds, exhibit significant removal by air stripping. Several PCB and pesticide compounds such as Toxaphene and Beta-BHC also show potential for volatilization during treatment. Acid extractables, on the other hand, are rarely stripped or volatilized from wastewater stored in impoundments or during activated sludge treatment. However, studies with solvent extracted fixed-bed gasifier quench liquors have indicated that phenol will be air stripped from wastewaters that are applied to evaporative cooling towers as makeup water. It appears that most of the compounds which may be air stripped have Henry's law constants greater than 10^{-3} atm m^3/mole.

Of the compounds and groups listed above, several are suspected to be present in wastewater from the synthetic fuels industries of interest. These

are benzene, ethylbenzene, toluene, phenolics, and certain polynuclear aromatic hydrocarbons. It should be noted that the presence of some of these compounds is suspected but not confirmed analytically. It is more likely that the volatile fraction (EPA 624) compounds will result from the upgrade of synthetic fuels to more conventional sources of energy (e.g., gasoline, kerosene). Halogenated priority pollutants are not expected to be found in wastes from these industries, since halogenation is not a reaction used in production of alternate fuels. However, they do result from the production of petrochemicals using conventional petroleum feedstocks.

Wastewater purification processes which may provide a release of air pollutants during treatment are equalization facilities and activated sludge processes which use surface impoundments for storage and treatment of aqueous wastes. Since the petroleum industry uses both of these in treating its wastewater, it is likely that both tar producing and non-tar producing coal gasification facilities will also.

Secondary treatment (i.e., activated sludge) processes will probably not be common in the oil shale industry because the wastewaters are likely to be used to quench and moisten the processed shale. However, the presence of volatile organics might preclude the use of wastewaters for this purpose, since any vaporized water and organics would directly enter the atmosphere. It should be noted that, at this time, wastewater data for the oil shale industry are based on computer models, laboratory experiments, and pilot-plant information. The presence of volatile organics has not been confirmed, nor has the use of equalization basins or activated sludge in wastewater treatment/management.

The magnitude of the problem concerning air emissions from wastewater treatment processes is unknown. Laboratory and bench-scale studies of the fate of pollutants in industrial wastewaters are not available. Analysis of wastewater streams from the industries of concern is also needed before the problem and the need for control strategies can be assessed.

SECTION 3

STUDIES ON TOXIC ORGANIC EMISSIONS FROM WASTEWATER TREATMENT PROCESSES

EMISSION MODELS

Many studies on volatile air emissions have been performed and reported in literature. Various authors have derived models which can be used to approximate hydrocarbon emissions from surface bodies of water. Others have either attempted to simplify these models or increase their accuracy. Many researchers have compared actual emissions with the emissions predicted using one or more of these models. The purpose of this section is to present the available models, their possible uses, limitations, and correlations with actual data.

The two most often cited models are those of Thibodeaux et al. (1, 2, 3, 4, 5, 6, 7) and Mackay et al. (8, 9, 10, 11). Both are based on the classical two-film concept of interphase mass transfer. Gas and liquid film mass transfer coefficients can be obtained from experimental data, literature, or calculated from literature correlations. Shen (12) provides correlations for estimating gas and liquid mass transfer coefficients (using Henry's law constants), diffusivities, viscosities, and densities. Roberts and Daendliker experimentally determined mass transfer coefficients as a function of agitation for several organic compounds (13).

The model by Thibodeaux is designed for modeling organic emissions from aerated and non-aerated surface impoundments. It may be used for estimating the maximum emission rates of individual compounds which can be volatilized.

It also applies only under steady-state conditions, where the bulk properties of flow and concentration do not change appreciably with time.

The model is limited in that it does not account for competition or interactions between other compounds, but only estimates emission rates of individual compounds. One way of using the model to estimate total hydrocarbon emissions may be to select a compound representative of a class of similar compounds and calculate its maximum emission rate. Selecting several classes and summing the emissions of each representative compound may give a reasonably accurate estimate of the total hydrocarbon emissions. Examples of classes and representative compounds are as follows (1):

Class	Compound
Paraffins	Hexane
Olefins	Butene
Aromatics	Toluene
Halogenated hydrocarbons	Methylene chloride
Oxygenated hydrocarbons	Acetone

Another limitation of this model is that it does not account for the competitive interactions between biological oxidation, adsorption onto the sludge, and volatilization into the air. It is merely a maximum estimate of air emissions. It is more suitable for use in designing an air-stripping process than in estimating organic emissions from a biological treatment system.

The model by Mackay has been developed for estimating unsteady-state emissions from non-aerated surface impoundments. An unsteady-state system is one which receives intermittent or varying waste flows so that the compositions in the air and impoundment vary with time. The Mackay model assumes well-mixed bulk air water systems with nearly stagnant films on either side of the interface. It does not account for the effects of turbulence, thermal

gradients, or surface wave action. The model would probably underpredict emission if these conditions are present in the impoundment (1).

This model may be used to approximate maximum rates of evaporative loss of low-solubility contaminants in an air-water system. It can be used to calculate emission rates for individual compounds; however, it cannot be conveniently used to estimate total volatile organic compounds (VOC) emissions from complex, multicomponent wastes. Estimation of the total VOC emissions may best be approximated by calculating emissions of representative compounds, as discussed previously with the model by Thibodeaux.

Neither the model by Thibodeaux nor Mackay have been widely tested. No actual data are available for comparison with predictions from these models. Their applicability, especially for design purposes, to treatment facilities containing complex, multicomponent wastes is not yet known.

Another predictive model developed by Mackay and Paterson (14) estimates the partitioning of substances in different phases (e.g., air, soil, water, biota, suspended solids, sediment) of the environment. It is based on a linear relationship between fugacity and concentration, where fugacity is a measure of the "escaping tendency" of a chemical substance from a phase.

This model may be used to predict the fate, concentration distributions, reaction characteristics, and persistence of chemicals released into the environment. However, it is necessary to assume volumes for each medium and an amount of solute in order to calculate partitioning. Also, as with the other models, the model estimates partitioning of individual compounds, rather than classes of compounds or total hydrocarbons.

A "typical" behavior profile as predicted by Mackay and Paterson (14) is a partitioning between water, sediment, atmosphere, and biota in the approximate proportions 20, 20, 60, and 0.1, respectively. The concentrations in

sediment and biota are approximately 500 and 1000 times those in the water column.

Other researchers have made an attempt to simplify the models of Thibodeaux, Mackay, and others. One correlation so developed is that of Truong and Blackburn (8) which incorporates Henry's law constants and air-flow-to-liquid-volume ratios to yield stripping rates directly. However, this correlation was developed for single component systems in pure water. Compounds tested individually were toluene, 1,4-Dichlorobenzene, methyl ethyl ketone, and phenol. The presence of surfactants, oils, salts, and non-volatile biomass was found to vary the stripping rate.

The stripping rates predicted by this model for several other compounds were compared with rates calculated from reported data. In the comparison of complete mix systems, the percent deviation between predicted and reported stripping rates ranged from 5% for 1,2-Dichlorobenzene to 76% for tetrachloroethylene, with the mean being 33%. Stripping rates from plug flow systems were also compared. In this case, the percent deviation between predicted and reported rates ranged from 6% for Dibromochloromethane to 99.4% for Tetrachloroethylene, with the mean being 86%. This correlation carried the same limitation as the model on which it was based: no consideration of the competitive interactions of biodegradation, adsorption, or stripping were involved.

In another study by Blackburn and Troxler (15) the Truong and Blackburn stripping correlation was tested experimentally along with other correlations for sorption and biooxidation. Seven compounds were used to test these correlations. Blackburn and Troxler summarized their research by saying that prediction of the fate of compounds using experimental data may be possible with further work. Prediction based on substrate properties was inconclusive and further work was recommended.

Research conducted by IT Corporation and the University of Tennessee (16) attempted to integrate existing knowledge and experimental data regarding

organic compound fate prediction in order to develop predictive models for the activated sludge process. Three separate approaches to fate prediction were investigated:

- Predictions based on experimental data;
- Predictions based on experimental data for surrogate compounds which are used to represent a class of compounds (e.g., the fate of toluene in an activated sludge process would be used to predict the fate of all aromatics); and
- Predictions based on a deterministic understanding of the fate mechanism and data on the physical, chemical, or structural properties of a specific compound.

The feasibility of each of these approaches is summarized in Table 1. However, in order to validate any of these approaches, further studies on contamination effects are needed for more compounds and activated sludge system configurations.

Other articles (17, 18) have been written attempting to apply these emission models to solid wastes which have been landfarmed or disposed of on land. These will not be discussed here since the primary emphasis of this report is volatile emissions from liquid waste treatment processes.

For the most part, the models available may be useful for emission inventory. However, much more work could still be done to develop a model to predict the actual fate of compounds and improving the accuracy of emissions inventories.

TABLE 1. FEASIBILITY OF ORGANIC COMPOUND FATE PREDICTIONS FOR ACTIVATED SLUDGE PROCESSES

Mechanism	Predictive Approach		
	Experimental Data for Specific Pollutant	Experimental Data for Surrogate Pollutant	Deterministic based on Compound Properties
Stripping	Feasible	Feasible with additional research	Feasible with additional research
Sorption	Probable with additional research	Probable with additional research	Probable with additional research
Biooxidation	Possible with additional research	Possible with additional research	Inconclusive-additional research needed to assess potential

Source: Reference 16

EXPERIMENTAL STUDIES ON THE FATE OF COMPOUNDS DURING ACTIVATED SLUDGE TREATMENT

Several bench-scale research studies have been performed to attempt to determine the fate of toxic compounds during activated sludge treatment. Researchers have studied air stripping by itself as one mechanism of removal. Others have studied competitive interactions between stripping and biodegradation. Some projects have also studied the adsorption of these compounds on waste biosludge.

The purpose of some researchers in studying air stripping of organics has been to evaluate it as a means of treatment for removal of organics prior to biological treatment processes. Their concern is mostly for the reduction of the organic content of treated water which is released into the environment. A few of the studies performed with this objective are those of McCarty (19), Ervin, Mangone, and Singly (20), and Raczko, et al. (21). Kincannon and Stover (22) also studied air stripping in a sterile environment prior to their experiment studying removal by both air stripping and biodegradation. In general, compounds having Henry's law constants above 10^{-3} atm m^3/mole are removed by air stripping (19).

Studies that have observed the interactions between stripping and biological oxidation include those of Kincannon and co-workers (22, 23, 24, 25, 26), Freeman et al. (27), and Strier and Gallup (28). Many of these have also studied adsorption onto sludge as a removal mechanism (25, 27, 28). Kincannon and Stover (22) experimented with synthetic wastewater containing a selected priority pollutant. Results from both sterile and biologically active systems were obtained for 15 pollutant compounds. A list of compounds which were stripped in a sterile system yet preferentially biodegraded in a microbially active system are presented in Table 2. Off gas compositions were measured to obtain the percent stripped. In the biologically active system, greater than 99.7% of the compounds were removed. The only two removal mechanisms operating were assumed to be air stripping and biological oxidation.

TABLE 2. FATE OF CERTAIN COMPOUNDS IN STERILE AND BIOLOGICALLY ACTIVE SYSTEMS

Compound	Influent Conc. (mg/L)	% Stripped Sterile Sys.	Influent Conc. (mg/L)	% Stripped Bio. Act. Sys.[a]	Henry's Constant ($atm\ m^3/mole$)
Acrolein	314	62.4	62	0	0.000097
Acrylonitrile	241	75.9	152	0	0.000063
Methylene Chloride	342	99.4	180	6.8	0.0025
Ethyl Acetate	288	81.5	167	6.5	[b]
Benzene	263	99.3	153	15.8	0.0046
1,2-Dichlorobenzene	72	85.3	83	21.7	0.0021

[a]In all cases over 99.7% of the pollutant was removed with the remaining fraction biooxidized.

[b]Data not available.

Source: Reference 22.

Similar studies by Kincannon and Stover examined the same compounds in a similar setting (23, 24, 25). In these studies, the sludge was also analyzed to obtain the percent adsorbed. In addition, pollutants were added to the synthetic waste in groups of threes rather than individually. The off gas and sludge were analyzed to attempt to determine the fate of these compounds. Biokinetic constants (after Lawrence, McCarty, Eckenfelder, and Gaudy) were also determined in these studies.

Material balances around laboratory-scale activated sludge units developed by other investigators (16) revealed that the fates of phenol and aniline were almost identical, with greater than 99.8 percent of the parent compound biooxidized and stripping losses below detectable limits. Removal of these compounds from wastewater by sorption on activated sludge was found to be insignificant. Biological oxidation was also determined to be the major removal mechanism for toluene (16). The ability of the activated sludge process to biologically degrade toluene was found to be sensitive to deviations from steady-state operating conditions. Stripping was determined to be a secondary removal mechanism, with approximately 12 percent of the toluene stripped, on average. However, the amount of toluene stripped from solution was variable and correlated to the concentration of this pollutant in the aqueous phase (16). Pentachlorophenol was found to be resistant to biological oxidation and the compound did not strip from wastewater during activated sludge treatment (16). Sorption onto biosludge was determined to be the major removal mechanism with between 6 and 8 percent of the feed pentachlorophenol adsorbed to the waste biomass.

Table 3 presents the results from a study of the biological treatability of organic priority pollutants by Kincannon, et al. (25). The log of the octanol/water partition coefficient (P_{ow}) found in Table 3 is a measure of the partitioning of organic compounds between the liquid phase and particulate matter. It may be useful in estimating the percent sorbed. In Kincannon's study, the percent sorbed was determined by analyzing the waste sludge. The percent stripped was obtained by analyzing the off-gas concentration, while

TABLE 3. MECHANISM OF TOXIC ORGANIC COMPOUND REMOVAL

Analyte	Class	Henry's Law Constant (atm m^3/mol)	Log Pow	Influent Concentration (ug/L)	Single Units		
					% Stripped[a]	% Sorbed[b]	% Biodegraded[c]
Nitrogen Compounds							
Acrylonitrile	Volatile	0.000063	-0.14	152	d		99.9
Phenols							
Phenol	Acid	0.0000013	1.46	173			99.9
2,4-Dinitrophenol	Acid		7.53	96			99.3
2,4-Dichlorophenol	Acid	0.000042	2.75	75			95.2
Pentachlorophenol	Acid	0.0000071	5.01	8		0.58	97.3
Aromatics							
1,2-Dichlorobenzene	Base/neutral	0.0019	3.38	83	21.7		78.2
1,3-Dichlorobenzene	Base/neutral	0.0026	3.38	69			
Nitrobenzene	Base/neutral	0.000024	1.86	100			97.8
Benzene	Volatile	0.006	2.04	153	2		97.9
Toluene	Volatile	0.0059	2.69	59	5.1	0.02	94.9
Ethylbenzene	Volatile	0.0058	3.15	60	5.2	0.19	94.6
Halogenated Hydrocarbons							
Methylene Chloride	Volatile	0.0032	1.25	180	8		91.7
1,2-Dichloroethane	Volatile	0.0011	1.48	258	99.5	0.5	
1,1,1-Trichloroethane	Volatile	0.0049	2.17	118	100		
1,1,2,2-Tetrachloroethane	Volatile	0.00042	2.56	201	93.5		
1,2-Dichloropropane	Volatile	0.0028	2.28	182	99.9		
Trichloroethylene	Volatile	0.0012	2.27	95	65.1	0.83	33.8
Chloroform	Volatile	0.0034	1.97	35	19	1.19	78.7
Carbon Tetrachloride	Volatile	0.03	2.69	19	33	1.38	64.9
Oxygenated Compounds							
Acrolein	Volatile	0.000097	-0.9	62			99.9
Polynuclear Aromatics							
Phenanthrene	Base/neutral	0.00013	4.46	0.56			98.2
Naphthalene	Base/neutral	0.0012	3.37	6.9			98.6
Phthalates							
bis-(2-ethyl hexyl) Pothalate	Base/neutral		8.73	0.26			76.9
Other							
Ethyl Acetate				1.67	1		98.8

(continued)

TABLE 3. (continued)

Analyte	Influent Concentration (mg/L)	Combined Units		
		% Stripped[a]	% Sorbed[b]	% Biodegraded[c]
Nitrogen Compounds				
Acrylonitrile	31			90
Phenols				
Phenol	65			99.9
2,4-Dinitrophenol	32			99.2
2,4-Dichlorophenol	24.1			77.1
Pentachlorophenol	3.7			97.8
Aromatics				
1,2-Dichlorobenzene	10			99.9
1,3-Dichlorobenzene	20			
Nitrobenzene	37.5			33.8
Benzene	39	2		97.2
Toluene	16.8	6.2		93.7
Ethylbenzene	19.3	7.5		92.4
Halogenated Hydrocarbons				
Methylene Chloride	56	2		97.2
1,2-Dichloroethane	63	75		25
1,1,1-Trichloroethane	60	99.7	0.3	
1,1,2,2-Tetrachloroethane	52	96.2		
1,2-Dichloropropane	48	99.5		
Trichloroethylene	65.5	69.7		30.1
Chloroform	14	15	1.36	82.8
Carbon Tetrachloride	7	28	0.03	71.7
Oxygenated Compounds				
Acrolein	31			90
Polynuclear Aromatics				
Phenanthrene	0.56			94.7
Naphthalene	2.3			78.6
Phthalates				
bis-(2-ethyl hexyl) Phthalate	0.35			85.7
Other				
Ethyl Acetate	63			98.9

[a] Percent stripped was determined by analyzing off gases.
[b] Percent adsorbed onto sludge was determined by extraction or purging sludge samples.
[c] Percent biologically oxidized was assumed to account for the rest of the removal (calculated).
[d] Blank means parameter not detected.

Source: Reference 25.

the percent biodegraded was assumed to be the percent removed minus the percent sorbed minus the percent stripped. Results are presented from samples containing both individual compounds and groups of three compounds. The groupings used by Kincannon et al. are shown in Table 4.

Note that in these studies, the influent concentrations of pollutants are relatively low compared to the levels found in certain high-strength industrial waste (e.g., tar producing coal gasification wastewaters). In wastewater which contains concentrations higher than those examined here, the removal efficiency that results from biological treatment may not be as high. The biodegradation efficiency may be lower because of toxicity effects on the microbial population. This may cause certain compounds to bioaccumulate in the sludge. The true fate of pollutants at higher concentrations is uncertain at this time. Research with the fate of pollutants is required to document the extent of biodegradation of toxic organics in actual industrial effluents.

A study by Kincannon and Fazel (26) examined the potential for stripping of organic compounds during powdered carbon-activated sludge treatment. Their research concluded that the addition of powdered activated carbon to an activated sludge process improved effluent quality and reduced off-gas emissions for toluene, but had only a slight effect on ethylbenzene. They also found that air stripping accounted for virtually all of the removal of 1,2-dichloroethane from wastewater during activated sludge treatment, and the addition of powdered carbon only reduced off-gas emissions at high dosages. Only slight improvements in effluent quality were observed during the treatment of synthetic wastewater containing toluene, ethylbenzene, 1,2-dichloroethane and benzene with powdered carbon-activated sludge. There was virtually no improvement in 1,2-dichloroethane removal with this treatment process. However, a powdered carbon-activated sludge treatment process operated at a solids retention time of 12 days achieved lower effluent concentrations than a process operated at a 3 day solids retention time. The authors concluded that a combination of a closed bioreactor system and the addition of activated

TABLE 4. TEST UNITS CONTAINING COMBINATIONS OF COMPOUNDS

Group	Compounds	Influent Conc. (mg/L)
I	Tetrachloroethane	52
	Nitrobenzene	37.5
	2,4-Dichlorophenol	24.1
II	Acrylonitrile	31
	Acrolein	31
	1,2-Dichloropropane	48
III	Benzene	39
	Methylene Chloride	56
	Ethyl Acetate	63
IV	Phenol	65
	1,2-Dichlorobenzene	10
	1,2-Dichloroethane	63
V	2,4-Dinitrophenol	32
	1,3-Dichlorobenzene	20
	1,1,1-Trichloroethane	60
VI	Pentachlorophenol	3.7
	Trichloroethylene	65.5
	Bis-(2-ethylhexyl) phthalate	0.35
VII	Toluene	16.8
	Ethylbenzene	19.3
	Phenanthrene	0.56
VIII	Chloroform	14
	Carbon Tetrachloride	7
	Naphthalene	2.3

Source: Reference 25.

carbon during biological treatment is an effective means of reducing the emission of volatile pollutants that are subject to biodegradation.

A study by Freeman, et al. (27) obtained results similar to those of Kincannon and co-workers. In Freeman's study, acrylonitrile was added to a bench-scale activated sludge system. The acrylonitrile concentration in the reactor was approximately 370 mg/L. Air, water, and sludge samples were taken and analyzed for the concentration of acrylonitrile. Air samples from a sterile system were also obtained.

Freeman's results agree with those of Kincannon for a biologically active system (25). In a biologically active system, greater than 99.9% of the acrylonitrile was biodegraded. However, approximately 18% of the acrylonitrile entering the feed was stripped in a sterile system, as opposed to 75% in Kincannon's study. Acrylonitrile was not detected in the sludge in either study.

Petrasek et al. (29) have studied the adsorption of priority pollutants in municipal wastewater activated sludges. Twenty-two compounds were studied: 4 pesticides, 3 phenolics, 6 phthalates, and 9 polynuclear aromatic hydrocarbons (PAHs). The compounds were injected simultaneously at a concentration of 50 ug/L or greater into actual municipal liquid waste. Samples of primary sludge, return activated sludge, and activated sludge process effluent were analyzed for these pollutants. The results are presented in Table 5.

Large errors were reported in some cases for the percent mass recovered. The percent of the compounds which accumulated in the sludges ranged from 0.5% to 126%. No off gas samples were taken; therefore, the percentages removed by stripping and biodegradation were not determined.

The only pollutant which was studied by both Petrasek and Kincannon (25) was pentachlorophenol. Their results differed: 31% was reported to have accumulated in the sludge by Petrasek, while Kincannon showed that only 0.58%

TABLE 5. RESULTS OF GC ANALYSIS OF MUNICIPAL WASTEWATER AND SLUDGE FOR THE PRESENCE OF PRIORITY POLLUTANTS

Pollutant	Influent Conc. (ug/L)	Percentage in Primary Sludge	Percentage in Return Act. Sludge	Percentage in Act. Slu. Effluent	Percentage Total Mass Recovered
Pesticides/PCBs					
Arochlor 1254	<33.5	51	60	2	113
Heptachlor	31.5	33	35	7	75
Lindane	45.5	12	8	55	75
Toxaphene	<47.4	31	27	2	60
Phenols					
2,4-dimethylphenol	95.7	0	0.5	1.1	1.6
Phenol	261.3	4.4	0.8	5	10.2
Pentachlorophenol	7.6	26	5	81	112
Phthalates					
Bis-(2-ethylhexyl)-phthalate	51.7	63	39	21	123
Butylbenzylphthalate	33.5	119	7	4	130
Diethylphthalate	46.4	7	9	3	19
Dimethylphthalate	47.3	0.3	2	2	4.3
Di-n-butylphthalate	43.8	39	11	6	56
Di-n-octylphthalate	28.2	91	43	17	151
Polynuclear Aromatic Hydrocarbons					
Acenaphthene	39.8	41	4	3	48
Anthracene	34.8	67	5	3	75
Benz(a)anthracene	23.8	67	18	2	87

(continued)

TABLE 5. (continued)

Pollutant	Influent Conc. (ug/L)	Percentage in Primary Sludge	Percentage in Return Act. Sludge	Percentage in Act. Slu. Effluent	Percentage Total Mass Recovered
Polynuclear Aromatic Hydrocarbons (cont.)					
Chrysene	38.9	75	13	3	91
Fluoranthene	30.6	84	13	6	103
Fluorene	37.9	51	3	2	56
Naphthalene	76.7	22	0.5	1	23.5
Phenanthrene	40.4	59	1	3	63
Pyrene	30.4	107	7	6	120

Source: Reference 29.

accumulated. This discrepancy cannot be explained at this time, though some differences between the studies were noted. While Petrasek used actual municipal liquid waste, Kincannon used synthetic industrial waste which contained ethylene glycol, ethyl alcohol, glucose, glutamic acid, acetic acid, phenol, and inorganic salts. In Petrasek's study, the components were all injected simultaneously with influent concentrations between 7.6 and 261.3 ug/L. Kincannon and co-workers studied components individually, or in groups of threes, with influent concentrations between 260 and 258,000 ug/L.

Petrasek, et. al., also attempted to correlate the fraction of each compound in primary and waste activated sludge as a function of log P_{ow}. The partition coefficients may be a useful parameter for estimating partitioning of organic compounds in the primary sludge; however, results for partitioning to waste activated sludge were not as reliable. Correlation coefficients for a plot of the fraction of a compound in sludge vs. the partition coefficient were 0.71 for the primary sludge analysis and 0.66 for the waste activated sludge analysis. One possible explanation for this difference is that the varying ability of the microorganisms to metabolize the compounds may have complicated the data interpretation (29).

Sorption experiments conducted by IT Corporation and the University of Tennessee (16) to determine kinetic rate constants and equilibrium relationships for sorption onto biological solids concluded that a linear relationship exists between the water-biomass distribution coefficient and the octanol-water partition coefficient for phenol, 1,4-dichlorobenzene, and pentachlorophenol. Sorption kinetics were rapid for all three compounds, with phenol having the largest first order sorption kinetic rate constant. These data were analyzed using a model that hypothesizes that the concentration of lipids in biomass determines the rate of organic compound sorption onto biological material, and that the rate process can be predicted by the magnitude of the octanol-water partition coefficient. It is noted that if this hypothesis is correct, the partitioning of an organic compound between the

water phase and the biomass phase is an extraction process and the term "sorption" is incorrect.

The final study obtained through the literature search was that of Lurker et al. (4). The main objective of this study was to investigate some of the potentially controlling factors influencing the atmospheric release of volatile organic compounds from activated sludge sewage treatment processes. The two compounds studied were hexachlorobicycloheptadiene (Hex-BCH) and chloroform in simulated wastewater.

The bench-scale study indicated that an increase in the aeration rate increased the release rate to the atmosphere. Also, the presence of suspended solids, the concentration of detergents in the sewage, and the solubility of the pollutant in water were found to affect the release rate. Chloroform, the more water-soluble compound, was relatively unaffected by the concentrations of suspended solids and detergents in the wastewater. On the other hand, the water-insoluble Hex-BCH stripping rate was strongly dependent on suspended solids and detergent concentrations. An increase in suspended solids concentration depressed the stripping rate. However, the stripping rate was increased by an increase in the detergent concentration.

Another study examined the relative effects of various contaminants on the stripping rates for toluene, 1,4-dichlorobenzene, and methyl ethyl ketone in test contaminant systems as compared to pure water (16). The contaminants examined were salt, oil, surfactants, biomass, and foul condensate from a pulp and paper mill. Most contaminants caused a reduction in the stripping rate of the subject organic compounds. In no case was the effect more than ± 50 percent when compared with pure water (distilled or tap water). The variations seem to be the greatest for the compounds with higher Henry's law constants.

SECTION 4

PROCESS DESCRIPTIONS AND METHODS OF WASTEWATER TREATMENT

The industrial processes studied in this analysis by-product coke production, coal gasification, direct and indirect coal liquefaction, and shale-oil retorting. The coal gasification based indirect liquefaction processes described here are the Koppers-Totzek (KT) and Lurgi Gasification processes. The Exxon Donor Solvent Direct Coal Liquefaction process is described as an example of a direct liquefaction process. The oil shale retorting processes covered are the TOSCO II process, the Lurgi process, and the Modified In Situ (MIS) process.

BY-PRODUCT COKE PRODUCTION

Coke processes manufacture a high-purity carbon product (coke) from special grades of sub-bituminous coal. In addition to coke, by-product processes also recover the volatile gases released during the coking operation. These by-product gases are generally used to underfire the coke ovens and heat various furnaces throughout the steel plant. Coke production is closely linked to the iron and steel industry, since coke is primarily used as a reducing agent in the production of pig iron.

By-product coke production is a destructive distillation process. Slot ovens are charged with bituminous coal and heated in the absence of air to drive off the volatile components. The residual remaining in the ovens is coke. The volatile components are processed in the by-product plant where tar, light oil, ammonia, and H_2S are recovered, leaving clean coke oven gas.

Sources of wastewater in a by-product coke plant are 1) flushing liquor bleedoff, 2) final cooler water blowdown, and 3) light oil plant intercepting

sump water. Flushing liquor is used to shock-cool the foul gas leaving the oven. It is a mixture of coal moisture plus the condensate from the volatile products driven off during the coking process. It contains pollutants such as ammonia, oil and grease, sulfides, cyanides, and phenols. This stream will likely have a high organics content. Phenols are present in quantities large enough to make recovery practical.

The second source of wastewater, the final cooler water blowdown, is the condensate resulting from cooling the saturated gas with direct contact cooling water. It is one of the major sources of hydrogen cyanide in the wastewater. It also contains ammonia, phenols, sulfide, thiocyanate, and organics. In some plants, this stream is used for make up water for coke quenching.

The final source of wastewater is the light oil plant intercepting sump water. This is the condensed process steam used for stripping the light oil from the wash oil. It also contains the process water additions at the decanter and miscellaneous water used for cleaning process tanks. Typical pollutants found in this waste stream are BOD, COD, TOC, cyanides, ammonia, oil, and phenols. Most plants discharge intercepting sump water to the quenching station for use as make-up water.

Wastewater streams which are not used for make-up water are usually combined for treatment. Biological treatment processes such as activated sludge ponds are most commonly used. Some plants may also employ stripping processes for the removal of ammonia and sulfides.

Table 6 presents estimated raw waste loadings of several pollutants. The exact nature of the organic wastes pertaining to classification by specific compounds is unknown. It is known that naphthalene is present in relatively large concentrations so that it must occasionally be skimmed off the surface of settling basins (30).

TABLE 6. ESTIMATED RAW WASTE LOADS IN THE BY-PRODUCT COKE INDUSTRY

Pollutant	Raw Waste Load[a]	Calculated Concentration[b]
Flow - m^3/metric ton coke	0.73	—
pH	6-9	—
Suspended Solids	65.5	90
Ammonia	1460	2,000
Phenol	263	360
Cyanide	146	200
BOD_5	876	1,200
Sulfide	292	400
Oil & Grease	87.5	120

[a] kg/1000 metric tons coke except where otherwise noted.
[b] mg/L.

Source: Reference 30.

LURGI COAL GASIFICATION/INDIRECT COAL LIQUEFACTION

The operations and processes which are described in this section are characteristic of coal-based synthetic fuels facilities which use dry ash Lurgi gasifiers to generate a raw synthesis gas. This synthesis gas can in turn be used to produce substitute natural gas or liquid fuels in an indirect liquefaction process. Indirect liquefaction will be the focus of this section.

Coal is prepared to gasifier feed specifications and gasified. The dry ash Lurgi gasifier is a medium pressure (2.1 to 3.2 MPa), moving bed gasifier operating below the coal ash fusion temperature. Coal is fed to the gasifier by a pressurized coal lockhopper above the gasifier, while steam and oxygen are fed into the bottom of the gasifier as reactants. The coal descends through the gasifier for a period of several hours, passing through zones of increasing temperature. The increasing temperature and reaction with steam and oxygen cause drying, devolatilization, gasification, and eventually combustion of the coal. The ash passes through a revolving grate at the base of the gasifier and into the ash lockhopper. The ash is then discharged into the ash quench system and transported in a slurry to a clarification system.

The hot crude gas leaving the gasifier is composed primarily of hydrogen, carbon monoxide, methane, and unreacted steam. It also contains high molecular weight organics (e.g., tars, oils, phenols), reduced sulfur and nitrogen compounds (e.g., H_2S, COS, mercaptans, NH_3, HCN), low molecular weight hydrocarbons (e.g., C_2 - C_5, benzene, toluene), and entrained coal dust.

The crude product gas is purified and upgraded to form a synthesis gas. The first step in this process is usually quenching or cooling. This removes condensible organics, moisture, entrained particulates, and water soluble organics. Next, if a certain ratio of hydrogen to carbon monoxide is required for product synthesis, the water-gas shift conversion ($H_2O + CO \longrightarrow CO_2 + H_2$) may be applied. Other necessary purification processes are acid gas

removal (AGR) and removal of trace sulfur compounds. AGR removes CO_2 and reduced sulfur compounds such as H_2S.

The moisture and heavy organics which condense from the crude gas as it cools produce a gas liquor stream. The gas liquor contains tars, oils, and phenols, as well as dissolved gases such as ammonia, sulfides, cyanides, and carbon dioxide. The tars, oils, and phenols are removed in the gas liquor separation unit. These by-products can be sold, used as fuels, or recycled to extinction. Ammonia and other by-products can be recovered from the stripped gas liquor. The upgraded and purified gas is usually used for synthesis of alternate fuels.

The clean synthesis gas (mostly CO and H_2) after shift conversion, acid gas removal, and sulfur removal can be used to make products for use as alternate fuels. Catalytic reactions are employed to produce either substitute natural gas, methanol, or liquid hydrocarbons (by Fischer - Tropsch synthesis or Mobil M-gasoline synthesis) from the gas.

The crude liquid fuel products of the Fischer-Tropsch (F-T) and Mobil M-Gasoline synthesis processes will require upgrading before marketing. The upgrading process for the F-T and Mobil M products are currently available in the petroleum refining industry. Potential processes include 1) HF alkylation of the C_3 - C_4 fraction to yield gasoline - blend hydrocarbons and commercial grade LPG, 2) hydrotreating for destruction of olefins and oxygenated organics, 3) catalytic reforming to produce more cyclic and branched-chain hydrocarbons, 4) C_5/C_6 isomerization to increase the anti-knock quality of pentanes and hexanes, and 5) catalytic polymerization to convert propene/butene fractions into higher molecular weight gasoline blending compounds.

Wastewater streams are contributed by the main process train, the auxiliary processes (regeneration & cleaning), and the pollution control processes. The primary waste streams are gas liquor, condensates, still bottoms from the

AGR system, synthesis process wastewaters (e.g., those from methanol, F-T, and Mobil M synthesis), gasifier ash quench blowdown, boiler and cooling tower blowdown, process equipment cleaning wastes, and Stretford (or similar) blowdowns, purges, and condensates. Potential pollutants are suspended solids, dissolved inorganics (NH_3, CO_2, H_2S, trace metals), suspended tars and oils, dissolved organics (phenols, organic acids, alcohols, other hydrocarbons), and inorganics such as sulfites, sulfates, thiocyanates, and polysulfates (31). Table 7 shows the pollutant concentrations in the gas liquor after several treatment processes.

Many of the pollutants found in these waste streams may be recovered as by-products. These include tars, naphthas, phenols, and ammonia. These by-products can either be sold or used within the plant. Other pollutants which must be removed include dissolved gases (H_2S, CO_2), dissolved organics, residual organics, and dissolved inorganics.

The organics found in fixed-bed gasifier wastewaters are presented in Table 8 for the Chapman and Lurgi-type gasifiers. Both gasification processes utilize wet scrubbing and produce a cooled fuel gas, by-product tars and oils, and process condensate (wastewater) stream. The data indicate that the majority of the extractable organics are phenolics which account for about 99 percent of the total chromatographable organics. Methylphenols contribute the majority of the phenolics identified, with phenol the next largest contributor. Of the base/neutrals, the compounds present in the greatest concentrations are indoles and the naphthalenes. The volatile organic compounds were identified at concentrations generally 2 to 4 orders of magnitude lower than the extractable compounds (32, 33).

The treatment of gas liquor, which is the major wastewater stream from a Lurgi gasification/indirect liquefaction operation, may require several units. The removal of suspended solids, tar, and oil is usually performed first.

TABLE 7. POLLUTANT CONCENTRATIONS IN INFLUENT AND TREATED WASTEWATER OF LURGI-BASED INDIRECT COAL LIQUEFACTION TREATMENT PROCESSES

Analyte (Concentrations in mg/L)[a]	Gas Liquor	Effluent from Bulk Organics Removal	Effluent from Dissolved Gas Removal	Effluent from Dissolved Organics Removal	Effluent from Residual Organics Removal
Flow Rate (m^3/hr)	304	293	293	292	291
COD	22800	22800	12320	12320	2460
BOD	10600	10600	3090	3090	310
TOC	7640	7640	4230	4230	850
Phenol	4540	4540	290	290	15
Organic Acids	2000	2000	1700	1700	85
Tars and Oils	150	150	50	50	15
CN^- (as HCN)	5	5	5	2.5	0.75
SCN^-	6	6	6	6	1.8
NH_4^+ (as NH_3)	7610	7610	7610	150	5
Cl^-	25	25	25	25	25
$CO_3^=$ (as CO_2)	13600	13600	13600	0	0
$S^=$ (as H_2S)	55	55	55	1	1
TDS (non-volatile)	2480				
pH	8.2				

[a]Except as noted.

Source: Reference 31.

TABLE 8. ORGANICS IN FIXED-BED COAL GASIFICATION WASTEWATERS[a]

Gasification System	Chapman		Lurgi-type at Kosovo
Wastewater Type	Separator Liquor		Phenosolvan Inlet Water
Sample Type	Average[b]	Range	grab
Acid Extractable Compounds			
Phenol	2,400	1900-3400	690
Methylphenols	3,200[c]	1500-4700	--[d]
Dimethylphenols(total)[e]	1,200	330-1900	333
2,4-Dimethylphenol	420[f]	98-820	130
Trimethylphenol	0.82	0.35-2.2	ND[g]
Indanol	1.7	<0.07-3.2	ND
1-Naphthol	5.0	3.3-8.5	ND
2-Naphthol	6.7	5.4-9.2	ND
Resorcinol/Catechol	30	3.6-65	ND
Hydroxybenzaldehyde	5.7	<0.18-19	ND
o-Cresol	--		260
m-Cresol	--		610
p-Cresol	--		100
Total Unknown Phenols	--		698
Base-Neutral Extractable Compounds			
Naphthalene	8.6	1.6-17	ND
Acenaphthalene	3.6	1.2-<6	ND
Fluorene	2.6	0.28-<6	ND
Phenanthrene/Anthracene	2.3	0.7-<6	ND
Fluoranthene	5.7	0.3-<9	ND
Pyrene	5.7	0.4-<9	ND
Bis(2-ethylhexyl)phthalate	12	1.2-32	ND
Chrysene	0.12		ND
Benzo(b)fluoranthene	0.10		0.19
Benzo(a)pyrene	0.12		28
Pyridine	1.2		46
Ethylpyridine(s)	18	1.3-41	5
Quinoline	3.1	0.62-5.6	ND
4-Methylquinoline	0.11		ND
1-Methylnaphthalene	2.3	0.43-4.2	ND
2,3-Dimethylnaphthalene	2.3	0.65-<4.5	ND
2,6-Dimethylnaphthalene	2.2	<1.3-<3	ND
Indole	12	8-14	ND
2-Methylindole	12	2.2-16	ND
3-Methylindole	2.4	0.58-3.6	ND
Diethyl phthalate	ND		ND
Di-n-butyl phthalate	ND		29
2-Methylpyridine	--		13
3- and 4-Methylpyridine(s)	--		26
Alkylpyridine(s)	--		12
Alkylquinoline(s)	--		0.92
Benz(a)anthracene	--		0.23
7,12-Dimethylbenz(a)anthracene	--		0.68
Benzo(b)fluoranthene	--		<0.004
3-Methylcholanthrene	--		0.02
Dibenz(a,h)anthracene	--		1.26
252 Group (as Benzo(a)pyrene)	--		
Volatile Organic Compounds			
Benzene	0.63	0.56-0.74	0.9
Toluene	0.42	0.38-0.46	0.5
Ethylbenzene	0.048	0.022-0.106	ND
m,p-Xylene	0.15	0.124-0.172	ND
o-Xylene	0.28	0.034-0.184	0.8

[a] All data as mg/L.
[b] Average of grab samples.
[c] One data point not included in the average was rejected due to extremely high value, but compound was identified 6 of 6 times.
[d] Dashes mean parameter not analyzed.
[e] Includes 2,4-DMP.
[f] The portion of 2,4-DMP from the B/N fraction was estimated from the amount found in the acid fraction.
[g] ND means not detected.

This may be accomplished by any of the following processes: gravity separation, air flotation, filtration, screening or coagulation/flocculation.

The next process unit usually removes bulk organics. The most common processes are solvent extraction units such as the Phenosolvan process. Wet air oxidation may also be used. Pollutants recovered by the Phenosolvan process include phenols and some organic acids. The phenols can be burned as a fuel within the plant.

Removal of dissolved gases usually follows the removal of bulk organics. Common processes used for this purpose are steam stripping, steam stripping with ammonia recovery (e.g., Phosam-W), vacuum distillation, and inert gas (i.e., nitrogen) stripping. These processes remove ammonia, hydrogen sulfide, and carbon dioxide, as well as some hydrocarbons. Naphthas can be recovered as a by-product from the Phosam-W process, as well as ammonia.

After the useable by-products have been recovered, the wastewater is usually biologically treated for the removal of dissolved organics remaining in the wastewater after pretreatment. Possible biological processes that can be used include activated sludge, trickling filters, aerobic lagoons, and waste stabilization pond treatment. Next, the residual organics can be removed in a polishing step. Activated carbon adsorption or chemical oxidation, are commonly used processes. The treated wastewater is usually disposed of by discharge to a receiving water body or reused as cooling tower makeup.

Other waste streams produced in the gasification/liquefaction operations are of minor importance and may be treated in units similar to those used for gas liquor. Some streams may be combined for treatment. The wastewater treatment processes which will be used in commercial scale facilities are unknown at this time, since such facilities are only in developmental and planning stages. Further discussion of these streams is beyond the scope of this report.

Other major wastewater streams are produced by the upgrading processes for the F-T and Mobil M-gasoline liquid products. Since the upgrading technology is likely to be borrowed from the petroleum refining and petrochemical industries, wastewater will probably be similar in nature also. Wastes from the petroleum industry contain volatile organics as well as base/neutral and acid extractable pollutants (34, 35, 36). Thibodeaux analyzed samples from several refineries and found that approximately 50% of the organics in petroleum wastewater are volatile (37).

Raphaslian and Harrison analyzed composite samples of wastewaters from a Class B petroleum refinery. Solvent extracted neutral, acidic, and basic fractions from the wastewater were analyzed. Over 300 compounds were identified in the neutral fraction from the wastewater based upon GC retention time and presence of major ions in mass spectral scans. The majority of the compounds identified were aromatic and alkylaromatic types (38).

Table 9 lists several priority pollutants and their concentrations which have been found in appreciable quantities in petroleum wastewater. Table 10 lists specific organic compounds which may be present in wastes from the petrochemical industry. No data on the concentration of these compounds are available. It should also be noted that the chlorinated organics found in petrochemical wastes will probably not be found in the synfuels industry. Chlorination processes will not be used in this industry unless the emphasis changes from production of alternate fuels to producing petrochemical products.

The treatment of synthesis waste, which is similar to petroleum waste, is usually not as complex as gas liquor treatment. A typical treatment scheme for petroleum wastewaters includes an API separator or a similar oil/water separator as the first unit. Steam stripping is used for hydrogen sulfide removal from certain process streams. Following these, biological treatment is most often used as the main process for removing organics from the wastewater.

TABLE 9. TYPICAL PRIORITY POLLUTANTS IN THE PETROLEUM REFINING INDUSTRY WASTEWATERS

Pollutant	Concentration (ug/L)
Benzene	>100
Ethylbenzene	>100
Methylene Chloride	>100
Toluene	>100
Phenol	250
2,4-Dinitrophenol	5600
4-Nitrophenol	2900
2-Nitrophenol	1400
2,4-Dimethylphenol	>100
2-Chlorophenol	315
Isophorone	3600
Naphthalene	302
Bis-(2-ethylhexyl) Phthalate	300
Benzo(a)pyrene	190
Anthracene	660
Fluorene	140
Phenanthrene	165

Source: Reference 34.

TABLE 10. TYPICAL PRIORITY POLLUTANTS IN THE PETROCHEMICAL INDUSTRY WASTEWATERS

Acrolein
Benzene
Carbon Tetrachloride
Chlorinated Hydrocarbons
Chloroform
Cresols
Cyanides
Dichloropropane
Ethyl Benzene
Ethylene Dichloride
Methyl Chloride
Phenolics
Polychloroethane
Toluene

Source: Reference 35.

After biological treatment, filtration can be used as a polishing step. Filtration removes suspended solids and the BOD/COD associated with this suspended material. Activated carbon systems may also be used as a polishing step to remove residual organics after biological treatment. Activated carbon is occasionally used as the major treatment process in a physical/chemical treatment system (34).

KOPPERS-TOTZEK COAL GASIFICATION/INDIRECT LIQUEFACTION

The Koppers-Totzek (KT) gasification process is different from Lurgi gasification. Not only are gasifier configurations different, but the operating conditions are as well. This results in very different wastewater streams. The Lurgi process produces a variety of organic compounds, but the KT process produces lower levels of non-methane organics.

The synthesis gas from each can be catalytically reacted to produce liquid products. The processes which upgrade and purify these products are similar; both borrow technology from the petroleum refining industry. Hence, both produce synthesis wastewaters similar in nature to those of the petroleum industry. Technologies for treatment of the wastewater are also presumed to be borrowed from the petroleum industry.

The KT gasifier is an entrained-flow slagging coal gasifier. It operates at a relatively low pressure, slightly above one atmosphere. Coal is combusted with steam and oxygen at a reactor temperature of 1510-1860 K, with a flame temperature range of 2000-2300 K. The reactor itself is a water-cooled steel vessel with a refractory lining. The most common configuration resembles an ellipsoid with horizontally opposing burners at the apices. A notable difference with the Lurgi gasifier is that of the residence time of the coal. While the Lurgi residence time is several hours, the KT residence time is a matter of seconds.

Coal is introduced continuously into the gasifiers through screw feeders at the burner heads. Partial oxidation reactions occur rapidly as the coal is entrained in a stream of high purity oxygen and low pressure steam. The coal residence time is less than one second. Raw product gas and entrained dust exit through the top of the gasifier and are cooled in a waste heat boiler. The molten slag exits through the base of the gasifier and falls into a quench tank.

The raw product gas must be purified and upgraded in order to be used for synthesis. After gas cooling and dust removal, NO_x is removed in a catalytic hydrogenation unit. The gas is compressed and cooled, then sent to a cyanide wash. Either water or cold methanol is used in the wash unit to remove hydrogen cyanide and residual ammonia present in the gas.

In addition, a shift conversion process is usually necessary before product synthesis. The KT gas contains hydrogen and carbon monoxide in a ratio of approximately 1:2. Product synthesis by the Fischer-Tropsch process requires a ratio of about 2:1.

Synthesis gas must also contain no more than a few percent CO_2. In addition, no sulfur may be present or the catalysts for the product synthesis will be poisoned. An acid gas removal process (e.g., Rectisol) is used to remove CO_2 and H_2S. Zinc oxide guard beds may also be used after the AGR process to remove trace sulfur compounds. Once the gas is purified, liquid products may be made from the gas by either methanol synthesis, F-T synthesis, or the Mobil M-gasoline synthesis.

The major waste streams produced by the KT process are quenched slag and transient waste gases. Wastewater streams contain mostly inorganics and are not produced in large quantities. The KT process is different from the Lurgi process in this respect, since the KT process produces low levels of non-methane organics. Most of the COD and BOD present in these wastes can be attributed to reduced sulfur and nitrogen species.

Liquid waste streams which are produced are 1) gas cooling/dust removal blowdown, 2) cyanide wash water (if water rather than methanol is used), 3) compression condensate, 4) synthesis condensate, 5) shift condensate, and 6) methanation condensate. Estimated pollutant concentrations are given in Table 11 for these streams. Liquid product upgrading will also produce waste streams; however, these are expected to be similar to those encountered in existing petroleum refineries.

The wastewater treatment processes used for treatment of liquid product upgrading wastes are also expected to be similar to those of the petroleum industry. A common scheme might be an API separator followed by biological treatment, such as an activated sludge process. Activated carbon and/or filtration may be used as polishing treatment steps.

Treatment schemes for KT liquid streams are similar to those of the petroleum industry. Since details of control schemes have not yet been proposed for KT-based indirect liquefaction facilities, only theoretical treatment schemes are available. Generally, the shift and methanation condensates are expected to be recycled to the plant as make-up water with little or no pretreatment. Hence, they will not be considered in the wastewater treatment scheme.

Three control examples have been evaluated by the Environmental Protection Agency. The streams considered for treatment are the synthesis condensate, the compression condensate, gas cooling/dust removal blowdown, and cyanide wash water. All three examples begin with flow equalization followed by activated sludge treatment. The first includes filtration and granular activated carbon units for polishing before discharge to surface waters. The second scheme requires only cooling tower concentration before discharging to a surface impoundment. The third treatment scheme includes cooling tower concentration, forced evaporation, and incineration before deep well injection (39).

TABLE 11. POLLUTANT CONCENTRATIONS IN WASTE STREAMS FROM THE KOPPERS-TOTZEK INDIRECT COAL LIQUEFACTION PROCESS

Analyte (Concentrations in mg/L)[a]	F-T Synthesis Condensate	Compression Condensate	Gas Cooling/ Dust Removal	Cyanide Wash H_2O
Flow Rate (m^3/hr)	160			
COD	12,000		100	
TOC	4,300		<10	
Phenols			<0.001	
Organic Acids	10,800			
Oil and Grease			1.3	
TDS			4,200	
NH_3		735	156	
CO_2		1,900		2,111
H_2S		48.7		176
CN^-		8.9	7	241
Cl^-		2,200	2,111	
$S_2O_3^=$		6.3	103	

[a]Except as noted.

Source: Reference 39.

EXXON DONOR SOLVENT DIRECT COAL LIQUEFACTION

Where the previously discussed processes converted coal first to a gas and then to liquid products, the Exxon Donor Solvent Direct Coal Liquefaction process converts coal directly to liquid products. The basic process maximizes the production of C_4^+ liquid hydrocarbons. The lighter, smaller hydrocarbons can be reformed to generate hydrogen for in-plant use.

Raw coal is crushed in the coal preparation area to minus 8 mesh and mixed with recycled donor solvent to form a slurry. The slurry is dried to less than 4.0 wt % moisture (on a dry coal feed basis). As the slurry is pumped to reaction pressure it is heated in a preheat furnace and mixed with heated hydrogen. The mixture enters the furnace which operates at 700 to 750 K and 13.9 MPa. In the reactor, coal is liquefied in the presence of molecular hydrogen and hydrogenated donor solvent. The solvent both dissolves the coal and donates hydrogen to the dissociated coal radicals. In the process, the donor solvent decomposes and becomes "spent".

The products from the liquefaction reactor are separated by vapor-liquid separation and distillation into several different streams. These include a light hydrocarbon gas stream, spent donor solvent, a C_3 liquefied petroleum gas (LPG), a C_4 LPG, a naphtha, fuel oil, and a heavy vacuum bottom stream. The light hydrocarbon gas stream is scrubbed with diethanolamine (DEA) to remove NH_3, H_2S and CO_2 and then passed through a steam reforming unit where hydrogen for the liquefaction step is generated. The spent donor solvent is hydrogenated in a fixed bed catalytic reactor and recycled back to the liquefaction reactor. The naphtha, fuel oil and LPG streams are stored as products. The heavy vacuum bottoms are fed to a Flexicoking unit (a proprietary process developed by Exxon) where steam and air are added to produce additional liquid products and a low-Btu fuel gas. In the Flexicoking unit, almost all the organic material in the vacuum bottoms is recovered as liquid products or fuel gas.

There are several wastewater streams produced which contain high concentrations of inorganic and organic pollutants. Most of these streams originate with the liquid product upgrading processes and are similar to those found in a petroleum refinery. Those which originate in the liquefaction process are the slurry drier cold separator wastewater and the liquefaction cold separator wastewater. Pollutants found in these two streams include NH_3, H_2S, CO_2, phenols, organic acids, COD, TOC, TDS, and HCl. Four streams originate from the product separation/purification process area. Several streams also originate from the liquefaction residue processing/hydrogen production process area. These streams also contain NH_3, H_2S, CO_2, phenols, organic acids, COD, TOC, TDS, and HCl. The streams containing organics are expected to be combined for treatment.

The EPA has evaluated four example schemes for treating the combined phenolic and sour wastewater streams from the Exxon Donor Solvent process. Table 12 presents the estimated characteristics of streams A and B of EPA's Integrated Control Example 1 (40). Stream A is a combined sour water stream. Stream B is a composite of the waste streams containing primarily dissolved gases. In Example 1, streams A and B are sent to an ammonia recovery unit and then to a phenol recovery unit. Stream C, the slurry dryer cold separator wastewater (a stream low in dissolved gases and dissolved organics), is combined with the wastewater leaving the phenol recovery unit. The combined wastewater is biologically treated in, for example, an activated sludge process. Filtration and activated carbon are applied as polishing treatments before the wastewater is discharged (40).

MODIFIED IN SITU OIL SHALE RETORTING

In situ retorting processes retort the shale underground, as do in situ coal gasification processes; however, modified in situ processes (MIS) require some mining in order to provide the needed void space in the underground retorts. Mining is also needed to create passageways for access to the retorts. The mined shale is brought to the surface and retorted by the

TABLE 12. POLLUTANT CONCENTRATIONS IN WASTE STREAMS FROM THE EXXON DONOR SOLVENT DIRECT COAL LIQUEFACTION PROCESS

Analyte	Stream A (kg/hr)	Stream B (kg/hr)	Stream C (kg/hr)
Flow Rate	26,000	131,000	156,000
COD	12,000	2	720
TOC	3,700	1	230
Phenols	2,400	1	150
Organic Acids	840	0	0
Oil and Grease	50	0	0
TDS	1,000	90	0
NH_3	3,600	3,000	12
CO_2	2,300	630	46
H_2S	4,700	170	1

Source: Reference 40.

Lurgi-Ruhrgas process. The Occidental Oil Shale, Inc. MIS process and its wastewater streams are discussed here, while a description of the Lurgi-Ruhrgas process follows in the next section.

Before MIS retorting, approximately 23% of the shale must be mined to create a void space. The Occidental MIS retorts are then formed by blasting a vertical section of oil shale, causing rubblized shale to drop into the void space. Air and steam are admitted at the top of the retort, above the rubblized shale, though a hot inert gas is initially introduced to begin start-up. When the temperature of the broken shale at the top of the retort is high enough, air is introduced to begin combustion. Steam promotes the water/gas shift reaction and provides a means of controlling the combustion zone temperature.

Four major reaction zones exist horizontally in an operating retort, each below the previous one. The uppermost zone is the preheat zone, where the air/steam feed gas is introduced and preheated through contact with hot processed shale. Below the preheat zone is the combustion zone, where oxygen is consumed by burning residual carbon in the processed shale.

In the retort zone, hot combustion gases heat the raw shale rubble to approximately 485°C. Here, true retorting occurs, where the kerogen is pyrolyzed to produce gas, oil, oil vapor, solid residue, and residual carbon. The products move downward by gravity into the cooling zone. Most of the vaporized oil condenses and mixes with condensed water vapor.

The resulting liquid oil/water stream flows from the bottom of the operating retorts into production-level drifts. The drifts are sloped, allowing the oil/water mixture to flow by gravity to oil/water sumps. The mixture is sent to a gravity separation unit where the oil and water are separated. The two resulting product streams are then pumped to the surface through independent systems. At the surface, final separation is performed in

oil-in-water and water-in-oil processes. Afterwards, the heavy oils are pumped to storage.

In addition to a liquid oil product, retorting also produces a retort gas mixture. It consists of light hydrocarbons from shale pyrolysis, carbon dioxide, water vapor, nitrogen, ammonia, and sulfur gases such as H_2S and COS. The retort gas is drawn to the surface by large blowers and fed to the gas treating equipment. The gas is first cooled, causing any water vapor present to condense. Next, ammonia and some acid gases (such as CO_2 and H_2S) are removed from the gas by an ammonia recovery unit, such as Phosam-W. The gas may then be treated for removal of H_2S or burned directly for steam and power generation.

The two major wastewater streams produced are the gas condensate and the retort water, which is produced in the oil/water product separation unit. The retort water contains dissolved gases and volatile organic compounds. It is usually treated by steam stripping to remove volatile compounds such as ammonia and H_2S. Table 13 contains average concentrations of some pollutants in MIS and Oxy-6 retort water (Oxy-6 is Occidental's MIS 6 process) (42). In addition, Table 14 lists some of the organic compounds which have been identified in ammonia-stripped retort water. After stripping, the retort water may be used in kettle evaporators to produce low quality steam for injection into MIS retorts. The overhead vapors from the stripper are sent to a Phosam-W (or other) ammonia recovery process and possibly to a desulfurization process.

The MIS gas condensate, which also contains ammonia and volatile organics, is passed through an oil/water separator to remove the lighter oil fractions. Afterwards it is sent to the Phosam-W unit for recovery of the dissolved ammonia. A portion of the treated water from the Phosam-W unit, termed stripped condensate, is recycled and sprayed into the upper portions of the absorber/cooler to promote scrubbing of the ammonia from the MIS retort gas. The rest of the stripped condensate may be used as boiler feedwater for the Lurgi-Ruhrgas process or sent to the kettle evaporators for raising low

TABLE 13. AVERAGE CONCENTRATIONS OF POLLUTANTS IN MIS RETORT WASTEWATER

Analyte	MIS Retort Water (mg/L)	MIS Gas Condensate (mass %)	Oxy-6 Raw Retort Wastewater (mg/L)	Oxy-6 Retort After NH_3 Stripping (mg/L)
COD	2,300-3,000	1.72	8,400-9,100	7,000-7,200
BOD_5	600			
DOC	800		2,800-3,300	2,200-2,300
Phenols	a		45	18-24
Organic Nitrogen			34	21
NH_3-N	9,600	1.39	1,100-1,250	7-40
NO_3-N			<1.0	<1.0
TDS	270	0.03	9,000-9,500	9,000-10,000
SCN			55-60	45-52
H_2S	125	0.01		
CO_2	14,400			
Alkalinity (as $CaCO_3$)	24,000		6,300-7,800	3,300-4,100
Color (Pt-Co units)			2,500	2,500
pH (units)			8.7	9.9-10.3
Volatile Organic Compounds	b	0.08		357
Acid Fraction Compounds				285
Base/Neutral Fraction Compounds				71
H_2O		96.77		

[a]Blank means data not available.

[b]90% of organic matter is volatile at 100°C.

Source: References 41 and 42.

TABLE 14. ORGANIC COMPOUNDS PRESENT IN OXY-6 RETORT WATER AFTER AMMONIA STRIPPING

Analyte	After NH_3 Stripping (Concentrations in mg/L)
ACID	
Carboxylic Acids	
C_1-C_5	40.71
C_6-C_{11}	113.38
Phenols/Cresols	28.27
Benzoic/Toluic Acids	11.42
TOTAL	193.78
BASE/NEUTRAL	
Cyclohexanones	0.44
Pyrroles	0.25
Pyrrolidinones (C_1-C_5)	5.54
Pyridines	0.13
Piperidinones	15.52
Quinolines	0.46
Cyclopentanopyrrolidinones	0.70
Cyclohexanopyrrolidinones	2.62
Cyclopentanopiperidinones	8.64
TOTAL	34.30
TOTAL (Acids + Base/Neutrals)	228.08

Source: Reference 42.

quality steam. The kettle evaporator concentrate may also be sent to an equalization basin and used to moisturize the Lurgi processed shale. Other streams which are also sent to the equalization basin and used for shale moisturizing are boiler blowdown, steam condensate, and mine water (41).

Data on concentrations of pollutants in the steam condensate and the blowdown from the Lurgi waste heat boiler are not available at this time. Both contain organics and dissolved solids, though these are present at low levels (41). Mine water from draining of aquifiers contains mostly inorganic pollutants which are present only at low levels. These streams will not be addressed further in this report.

LURGI-RUHRGAS OIL SHALE RETORTING WITH OPEN PIT MINING

The Lurgi-Ruhrgas retorting process can be used either to retort shale mined by the open pit method or to retort the shale removed from an MIS process. In either case, the shale initially requires crushing and size reduction to less than 20 centimeters before retorting. Secondary and tertiary crushing further reduce the shale size to between 0.6 and 0.8 centimeters (41, 43).

After size reduction, the shale is fed through a feed hopper to a double screw mixer, where is it combined with a heat carrier in a ratio of 1:4 or 1:8 (mass of crushed shale: mass of heat carrier). Processed shale is usually used as the heat carrier, though sand may be added as a coarse-grained heat carrier when the amount of shale fines is too large. The heat carrier (650 - 700 °C) heats the entire mixture to approximately 500 - 540 °C within a few seconds.

At this temperature, retorting of the kerogen in the oil shale occurs, resulting in the production of retort gas, shale oil vapor, and water vapor. After partial retorting, the mixture of shale and heat carrier is dropped from

the screw mixer into surge vessels. Here, residual oils are removed by distillation.

Next, the shale residue and heat carrier are passed to the lower section of a lift pipe, where combustion air is introduced. Essentially all available organic carbon contained in the retorted shale residue is burned in the lift pipe. A moderate amount of carbonate decomposition also occurs in the shale.

At the top of the lift pipe, the hot processed shale is separated from the flue gases in the collecting bin. Fines are carried out of the bin with the flue gas stream, while the coarse shale residue accumulates in the lower part of the bin. When used as a heat carrier, the shale flows continuously to the mixer.

The pyrolysis products stream containing shale fines is withdrawn at the end of the screw mixer. The fines are separated by two cyclones in series and returned to the recycle system. The vapor stream then passes through a sequence of three scrubbing coolers. The first cooler removes dust and the heavier oil fraction, the second produces a water-free middle oil and the third produces an aqueous condensate and a light oil fraction. The light oils are separated from the aqueous condensate (gas liquor) in an oil/water separator. The gas liquor contains much of the ammonia and sulfur dioxide in the gas stream. The overhead from the third cooler is scrubbed with a lean oil in the naphtha scrubber to recover naphtha and any desirable condensible gases. Residual H_2S may also be removed from the noncondensable retort gas by one of several methods (e.g., Holmes-Stretford Gas Treating Process).

The primary wastewater streams associated with Lurgi-Ruhrgas retorting are the gas liquor and the compressor condensate. Both streams contain dissolved ammonia, sulfur compounds, and volatile organics, so they are combined for treatment. Table 15 shows the estimated composition of these streams. Most of the ammonia and volatile compounds are removed by an ammonia

TABLE 15. COMPOSITION OF WASTEWATER STREAMS FROM A LURGI-RUHRGAS RETORTING PROCESS

Analyte	Gas Liquor (mass %)	Compression Condensate (mass %)
H_2O	98	98
NH_3	0.59	0.45
CO_2	0.76	0.53
$(NH_4)_2SO_3$	0.13	0.76
Strippable Organics	0.02	-
Nonstrippable Organics	0.06	-

Source: Reference 43.

recovery process such as the Phosam-W process. The treated water is then used for moisturizing processed shale.

Process shale moistening may create a potential environmental concern if wastewaters containing any volatile organic matter are used. The hot processed shale must be quenched before being disposed. The stripped foul water is expected to be used for this purpose. Any volatile organics present in the quench water will be volatilized and lost to the atmosphere during quenching. In addition, prior to use as moisturizing/quenching water, wastewater streams are usually combined in an equalization basin. Potential may exist in these impoundments for volatilization of organic compounds into the atmosphere. No studies have yet been performed to assess the potential of VOC emissions from wastewater handling facilities associated with the oil shale retorting industry (43).

TOSCO II OIL SHALE RETORTING PROCESS

The TOSCO II process is similar to the Lurgi-Ruhrgas process in that both are indirectly heated by solid-to-solid heat exchange. However, where the Lurgi process uses recycled shale to provide the heat of retorting (41), the TOSCO II process uses hot ceramic balls. The process description and wastewater treatment scheme which follows has been proposed by the Colony Development Operation (44).

Mined oil shale is crushed to less than 1.3 centimeters and preheated to 260°C with hot flue gases from the ball heater. The preheated raw shale and ceramic balls, which have been heated to about 700°C, are combined and added to the retort in a mass ratio of 1:1.5, respectively.

The raw shale is pulverized by the rotating action while mixing transfers heat from the ceramic balls to the shale. The shale temperature is raised to approximately 480°C, at which temperature retorting of the shale occurs. The main product of retorting is a retort gas.

Following retorting, the gas product, ceramic balls, and retorted shale are sent to an accumulator vessel. The accumulator is a rotating screen or trommel which retains the balls but allows the pulverized shale to pass through. The ceramic balls are cleaned and recycled in another unit. The processed shale is cooled, moisturized to approximately 14% water by weight, and transported to the disposal area. The retort gas is removed from the vapor dome at the top of the accumulator and sent to the oil recovery section. There, the retort gas is separated by fractionation into a gas, naphtha oil, gas oil, bottom oil, and gas condensate.

The retort gas is further fractionated into a C_2 and lighter fraction and a C_3/C_4 fraction. These streams are treated for acid gas removal by diethanolamine (DEA) in separate absorbers. The C_2/lighter fraction is used as plant fuel and for steam reforming. The C_3/C_4 stream is split into a C_3 fraction which is sold and a C_4 fraction for in-plant consumption. The regenerator overhead gas is sent to a Claus sulfur recovery unit and then to a Wellman-Lord unit, which converts most of the sulfur compounds to SO_2.

The naphtha and gas oil are hydrotreated with hydrogen from steam reforming. Hydrotreating also reduces nitrogen and sulfur to ammonia and hydrogen sulfide, which are removed by a water wash. The wash water or sour water is treated in an ammonia recovery unit such as a Phosam-W unit. The stripped sour water is recycled back to the hydrotreaters for reuse as wash water. The overhead gas from the ammonia recovery unit is sent to the Claus unit for recovery of sulfur.

The bottoms oil is coked to produce gas, naphtha, gas oil, and coke. The coke is disposed of with the processed shale, since it is unlikely that there will be a commercial market for it. The other product streams are sent to their respective treatment or upgrading units. Foul water produced by condensing steam in the coking process is combined and treated with the gas condensate.

The gas condensate and the sour water produced in the gas oil hydrotreater are the major wastewater streams produced by the TOSCO II retort. Table 16 lists the composition of these streams before and after treatment.

The sour water is sent to an ammonia recovery process such as the Phosam-W unit. Gas condensate is steam stripped to remove dissolved ammonia, H_2S, and organics. Stripped sour water is recycled back to the hydrotreater for reuse as wash water. The stripped foul water, which still contains a significant amount of dissolved organics, is used for process shale moistening.

As with the MIS/Lurgi and Open Pit Mining/Lurgi processes, moistening of processed shale from the TOSCO II process may cause an environmental concern. Any volatile organic matter present in the wastewater will probably volatilize during quenching. Equalization basins used to collect wastewater for quenching may also allow volatilization of organics into the atmosphere.

One developer proposed that the stripped foul water be biologically treated prior to shale moisturizing in order to control organics. However, few data are available regarding the effectiveness of biooxidation processes for the removal of organics from oil shale wastewaters, and the estimated removal efficiency may be low (44). Should biological treatment be inefficient, aeration may also produce air emissions of some volatile organic compounds.

Organics removed from the wastewater streams are present in the overhead vapors from the stripper and the ammonia recovery unit. Both overhead streams are directed to the Claus unit for sulfur removal. The exact fate of the organics which are sent to the Claus unit is uncertain. They may either be

TABLE 16. ESTIMATED POLLUTANT CONCENTRATIONS IN WASTEWATER FROM THE TOSCO II OIL SHALE RETORTING PROCESS

Analyte	Sour Water (mg/L)	Stripped Sour Water (mg/L)	NH_3 Recovery Overhead (mass %)	Gas Condensate (mg/L)	Foul Water (mg/L)	Stripper Overhead (mass %)
NH_3	44,170	64	0.65	3,088	3,088	3.99
H_2S	20,910	19	62.30	[a]	1,945	2.66
CO_2	0	0	[b]	3,749	3,749	5.16
Organics	0	0		4,324	4,324	2.98
Phenols				510	510	
Acids				1,710	1,710	
Bases				680	680	
Neutrals				1,424	1,424	
TOC	na[c]	na		3,160	3,160	
H_2O	na	na	37.04	na	na	85.22

[a] No data are available for the estimated concentration of H_2S in the gas condensate, but it is calculated to be approximately five percent of the H_2S concentration in the foul water stream.

[b] Blank means parameter not present.

[c] na means not analyzed.

Source: Reference 44.

destroyed in the Claus process or exit the Claus unit in the tail gas, which is sent to the Wellman-Lord unit. Organics present in the tail gas will probably leave the Wellman-Lord unit and become feedstock to an emission control incinerator before they are discharged to the atmosphere (44). Therefore, these organic compounds will probably not be found in any wastewater stream.

SECTION 5

THE PRESENCE AND FATE OF VOLATILE ORGANIC COMPOUNDS IN WASTEWATERS FROM SYNFUELS INDUSTRIES

The assumed fate of groups of organic priority pollutants that results from treatment of wastewaters which contain the compounds are presented in Table 17. These estimates are the conclusions of Kincannon, et al. (25) and are based on experimental results. Based on the data found through the literature survey, many EPA priority pollutants present a potential concern due to volatilization and air stripping during wastewater treatment. Most of the volatile fraction pollutants (i.e., EPA Method 624) and several of the base-neutral fraction pollutants, particularly simple halogenated compounds, exhibit significant removal by air stripping. Several PCB and pesticide compounds such as Toxaphene and Beta-BHC also show potential for volatilization during treatment.

Table 18 lists the EPA organic priority pollutants for which Henry's law constants were available. It should be remembered that this approximation does not consider the concentration of the pollutant present in the wastewater. It also does not take into account any form of competition between biodegradation, adsorption, and stripping. It appears that most of the compounds which may be air stripped have Henry's law constants greater than 10^{-3} atm m^3/mole. Of this group, the compounds that have been most frequently detected in treated wastewaters from petroleum refineries are benzene, toluene, chloroform, methylene chloride, trichloroethylene, and ethylbenzene.

Of the compounds and groups listed above, several are suspected to be present in wastewater from the synthetic fuels industries of interest. These are benzene, ethylbenzene, toluene, phenolics, and certain polynuclear

TABLE 17. FATE OF TOXIC ORGANIC COMPOUNDS DURING WASTEWATER TREATMENT

Group of Compounds	Fate
Nitrogen Compounds (e.g., acrylonitrile)	Biological Oxidation
Phenols	Biological Oxidation
Oxygenated Compounds (e.g., acrolein)	Biological Oxidation
Polynuclear Aromatics (e.g., phenanthrene)	Biological Oxidation
Phthalates	Biological Oxidation
Aromatics with Henry's Law constant = 10^{-5} atm m^3/mole (e.g., nitrobenzene)	Biological Oxidation
Aromatics with Henry's Law constant $<10^{-5}$ atm m^3/mole (e.g., benzene)	Both Stripping and Biological Oxidation
Halogenated Hydrocarbons	Unpredictable

Source: References 25 and 45.

TABLE 18. HENRY'S LAW CONSTANTS AT 20 AND 25°C

Priority Pollutants	Henry's Law Constants 20°C (atm m^3/mole)	Henry's Law Constants 25°C (atm m^3/mole)
VOLATILES:		
Acrolein	0.000097	a
Acrylonitrile	0.000063	
Benzene	0.0046	0.00555
Carbon Tetrachloride	0.025	0.0302
Chlorobenzene	0.004	0.00393
1,1-Dichloroethane	0.0051	0.00545
1,2-Dichloroethane	0.0011	0.0011
1,1,1-Trichloroethane	0.0036	0.00492
1,1,2-Trichloroethane	0.0078	
1,1,2,2-Tetrachloroethane	0.00042	
Chloroethane	0.015	
Chloroform	0.0034	0.00339
1,1-Dichloroethylene	0.17	0.015
1,2-Transdichloroethylene	0.0057	0.00532
1,2-Dichloropropane	0.002	0.00282
1,3-Dichloropropylene	0.002	0.00355
Ethylbenzene	0.0057	0.00644
Methylene Chloride	0.0025	0.00319
Methyl Chloride	0.008	
Methyl Bromide	0.093	
Bromoform	0.00063	0.000532
Dichlorobromomethane		0.00212
Trichlorofluoromethane	0.11	0.0583
Dichlorodifluoromethane	2.1	
Chlorodibromomethane		0.000783
Tetrachloroethylene	0.023	0.0287
Toluene	0.0057	0.00593
Trichloroethylene	0.01	0.0117
Vinyl Chloride	6.4	
ACIDS:		
2-Chlorophenol	0.000021	
2,4-Dichlorophenol	0.000042	
2-Nitrophenol	0.000076	
4,6-Dinitro-o-cresol	0.00000017	0.0000041
Pentachlorophenol	0.0000021	
Phenol	0.00000027	0.0000013

(continued)

TABLE 18. (continued)

Priority Pollutants	Henry's Law Constants 20°C ($atm\ m^3/mole$)	Henry's Law Constants 25°C ($atm\ m^3/mole$)
BASE/NEUTRAL:		
Acenaphthene	0.00019	0.000241
1,2,4-Trichlorobenzene		0.00393
Hexachlorobenzene		0.0017
Hexachloroethane	0.0011	0.00985
1,2-Dichlorobenzene	0.0017	0.00194
1,3-Dichlorobenzene	0.0027	0.00263
1,4-Dichlorobenzene	0.0021	0.00272
Bis-(2-chloroisopropyl) Ether	0.00011	
Hexachlorobutadiene		0.0103
Hexachlorocyclopentadiene		0.0164
Isophorone	0.0000042	
Naphthalene	0.00036	
Nitrobenzene	0.000011	0.000024
Di-n-butyl Phthalate	0.000063	
Dimethyl Phthalate	0.00000042	
Acenaphthylene		0.000114
Anthracene	0.0014	
Fluorene	0.00021	0.000117
Phenanthrene	0.00013	
PESTICIDES:		
Aldrin	0.0021	0.000496
Dieldrin	0.00000017	0.000058
Chlordane		0.000048
4,4'-DDT	0.000034	
Heptachlor	0.0023	0.00148
Heptachlor Epoxide		0.000032
BHC-Alpha	0.00002	
BHC-Beta	0.011	
PCB-1242 (Arochlor 1242)	0.00049	
PCB-1254 (Arochlor 1254)	0.0023	0.00837
PCB-1248 (Arochlor 1248)	0.003	
PCB-1260 (Arochlor 1260)	0.0061	
Toxaphene	0.063	0.00489

[a]Blank means data not available.

Source: References 18, 19, and 42.

aromatic hydrocarbons such as naphthalene and phenanthrene. Other pollutants which are found in petroleum wastewater are listed in Table 9.

It should be noted that the presence of the volatile fraction (EPA 624) compounds is suspected but not confirmed analytically. It is more likely that the compounds will result from the upgrade of synthetic fuels to more conventional sources of energy (e.g., gasoline, kerosene). Halogenated priority pollutants are not expected to be found in wastes from these industries, since halogenation is not a reaction used in production of alternate fuels. However, they do result from the production of petrochemicals using conventional petroleum feedstocks.

Evaporative cooling tower studies conducted by the University of North Dakota with pretreated fixed-bed gasifier quench liquors (i.e., extracted with di-isopropyl ether to reduce phenols and steam stripped to reduce ammonia and remove acid gases) used as makeup water indicated the presence of phenol in the exhaust air. These tests reported average exhaust phenol levels that corresponded to a volatilization of greater than 90 percent of the influent mass of phenol. Although biological activity occurred in the pilot cooling tower, it was confined to the removal of organic acids in the wastewater (46). Studies with the biooxidation (e.g., activated sludge treatment) of fixed-bed gasifier wastewaters have generally reported that microbial activity is primarily responsible for the removal of phenol. Factors which effect the extent of biodegradation are likely to include microbial residence time, liquid residence time, pH, temperature, and the quantity of acclimated microorganisms. It would seem from the results of the University of North Dakota research that the physical conditions necessary for biodegradation of phenol are not conducive to the optimal operation of an evaporative cooling tower.

Since these compounds may indeed be present in wastewater from synfuels industries that are involved in the production of liquid fuels, it is important to know if environmental impacts are significant. Those wastewater processes which may provide a release of air pollutants during treatment are

waste equalization facilities and activated sludge processes which use surface impoundments for storage and treatment of aqueous waste. Since the petroleum industry uses both of these in treating its wastewater, it is likely that both tar producing and non-tar producing coal gasification facilities will also. Liquefaction facilities are also expected to use equalization ponds and aerobic biological treatment (40). The by-product coke industry currently uses activated sludge as its most common form of wastewater treatment.

In addition, oil shale retorting processes will probably use equalization basins. However, secondary treatment (i.e., activated sludge) processes will probably not be common in the oil shale industry. Currently, the developers plan on using the wastewater to quench and moisten processed shale. However, the presence of volatile organics might preclude the use of wastewaters for this purpose, since any vaporized water and organics would directly enter the atmosphere. It should be noted that, at this time, wastewater data for the oil shale industry are based on computer models, laboratory experiments, and pilot-plant information. The presence of volatile organics has not been confirmed, nor has the use of equalization basins or activated sludge in wastewater treatment/management.

The magnitude of the problem concerning air emissions from wastewater treatment processes is unknown. Laboratory and bench-scale studies of the fate of pollutants in industrial wastewaters are not available. Analysis of wastewater streams from the industries of concern is also needed before the problem and the need for control strategies can be assessed.

SECTION 6

DATA LIMITATIONS, GAPS, AND NEEDS

Several data limitations are identified by this study. Experimental data on the fate of organic priority pollutants during wastewater treatment are limited because only a few compounds have been studied. Most work so far has been with either laboratory or bench scale studies. Also, few researchers have used actual wastes for their experiments. Many use synthetic wastes which contain only one to three priority pollutants. The interactions between similar and dissimilar compounds have not been studied. In addition, the competitive interactions between different removal mechanisms (e.g., stripping, biodegradation, and adsorption) have also not been studied.

A large data gap is the lack of knowledge of the actual wastewater composition in the industries studied. Few analyses of individual compounds have been performed with wastewater from any of the synfuel direct and indirect liquefaction processes. Most available data are either design estimates or data from laboratory and pilot-scale systems. In addition, wastewater treatment schemes used for the various processes are still being planned.

More research is needed to determine the accuracy of the theoretical emission models. Research is also needed to study the fate of priority pollutants during wastewater treatment, especially with aerated activated sludge processes. There is a need for a controlled experimental environment to study the phase distribution of organics. Bench-scale testing of actual wastewater containing pollutants at concentrations similar to those found in industrial waste is needed. Air emissions from systems containing active organisms need to be measured, as well as the concentrations of the pollutants which accumulate in the sludge. If organics do bioaccumulate, the study of

the volatilization of these pollutants as a result of landfarming of the sludge should also be considered.

SECTION 7

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